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Metastable Behavior in Uniaxial Ferroelectrics TGS and TGSe near T_C

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High resolution hysteresis loops measurements in triglycine sulfate (ordinary critical point) and in triglycine selenate (tricritical point) allow the approximate characterization of the behavior in the metastable region ($E < 0$, $P > 0$, or vice versa) at $T \leq T_C$. The coercive field may be assumed to reflect three different regimes corresponding with three switching regimes. The observed coercive field seems to approach $E_C \approx \text{Const}(1 - T/T_C)^{\frac{3}{2}}$ for TGS and $E_C \approx \text{Const}(1 - T/T_C)^{\frac{5}{4}}$ for TGSe in the intervals $10^{-4} < (1 - T/T_C) < 10^{-3}$ and $10^{-4} < (1 - T/T_C) < 10^{-2}$, respectively.

I. INTRODUCTION

The theoretical description of the ferroelectric coercive field [1] and its temperature dependence is a very complex problem because one must take into account that moving down in a temperature away from $T = T_C$, successive mechanisms may be responsible for the polarization reversal associated with the coercive field. In addition, experimentally, the coercive field is strongly dependent on field amplitude, frequency and available range of circuit resistors for phase compensation, which complicates the choice of experimental conditions. In this work we have investigated the coercive field in triglycine sulfate (TGS) and triglycine selenate (TGSe) close to T_C and in a wide temperature range down to approximately midway to zero absolute temperature.

II. EXPERIMENTAL

The samples were small platelets, $112 \text{ mm}^2 \times 0.7 \text{ mm}$ for TGS and $28 \text{ mm}^2 \times 0.96 \text{ mm}$ for TGSe, in size, cut from a larger single crystal grown from water solution. Gold evaporated electrodes were deposited on the main surfaces. The temperature of the sample was controlled using a temperature controller (Unipan 680) capable of producing very slow linear heating and cooling ramps (6 K/h in our case). Hysteresis loops [2] were obtained using a DDP (Diamant-Drench-Pepinsky) circuit, with phase compensation only through the change of the auxiliary resistance. The loops were recorded in a relatively wide temperature interval below T_C for both crystals using a digital oscilloscope (Nicolet NIC-310). T_C is 321.25 K (± 0.05 K), for TGS, and 294.50 K (± 0.05 K), for TGSe, calculated from the fit to the P_s^2 vs. T for TGS and P_s^4 vs. T for TGSe. For each hysteresis loop, 4000 points were recorded at each temperature, which ensured high resolution of the P vs. E data. The

driving field was 5 kV/cm for TGS and 7 kV/cm in the case of TGSe, 150 Hz was the field frequency in both cases. A computer program was used to center the hysteresis loops to avoid the distortions due to spontaneous internal bias caused by charged impurities in the crystal.

III. RESULTS AND DISCUSSION

The generalized equation of state has the form [2]:

$$\frac{E}{\beta N \mu} = \frac{T}{T_C} \tanh^{-1} \left(\frac{P}{N \mu} \right) - \beta P \left(1 + \left(\frac{\gamma}{\beta} \right) \left(\frac{P}{N \mu} \right)^2 + \left(\frac{\delta}{\beta} \right) \left(\frac{P}{N \mu} \right)^4 \dots \right) \quad (1)$$

where E is the external field, P is the polarization, β is the dipolar effective field coefficient, N the number of elementary dipoles, μ , per unit volume, and γ, δ, \dots are the coefficients of higher order terms. Introducing $e = E/\beta N \mu$, $p = P/N \mu$, defining $g = \gamma/\beta (N \mu)^2$, and $h = \delta/\beta (N \mu)^4$, and expanding the hyperbolic tangent we get :

$$e = \left(\frac{T}{T_C} - 1 \right) p + \left(\frac{1}{3} \frac{T}{T_C} - g \right) p^3 + \left(\frac{1}{5} \frac{T}{T_C} - h \right) p^5 \dots (2)$$

This equation describes a theoretical hysteresis loop as shown in Fig. 1. In the case of TGS (ordinary critical point, $g < 1/3$) [2] we will take terms involving the first and third powers of p on the right side of Eq. (2). On the other hand in the case of TGSe (tricritical point, $g = 1/3$) [2] the term of third power in p goes to zero at $T \approx T_C$, so the fifth power must be taken into account. To determine the end of the metastable region in the vicinity of T_C , which defines the coercive field (see Fig. 1), we make use of the fact that at these points:

$$\frac{\partial e}{\partial p} = 0. \quad (3)$$

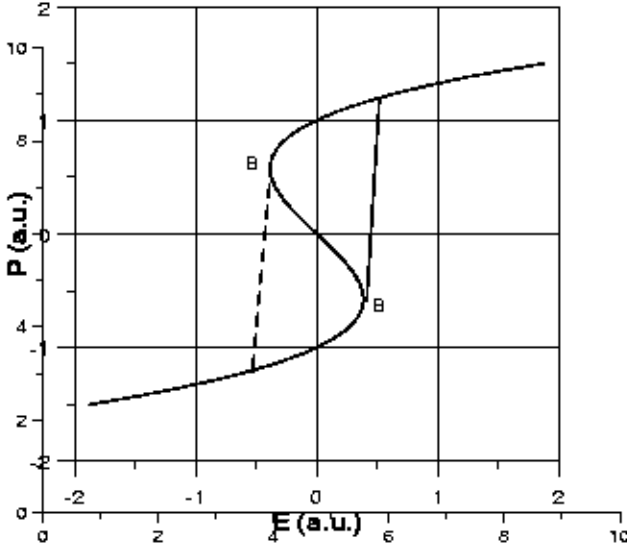


Fig. 1. Theoretical hysteresis loop, $P(E)$ in a.u. The point B corresponds to the definition of coercive field.

Using Eq. (3) for $T \approx T_C$, we get the polarization, p_C , at these points

$$p_C = \pm \left[\frac{1}{3(\frac{1}{3} - g)} \left(1 - \frac{T}{T_C} \right) \right]^{\frac{1}{2}} \text{ for TGS } (g < 1/3), (4)$$

$$p_C = \pm \left[\frac{1}{5(\frac{1}{5} - h)} \left(1 - \frac{T}{T_C} \right) \right]^{\frac{1}{4}} \text{ for TGSe } (g \approx 1/3). (5)$$

Substituting Eqs. (4) and (5) in Eq. (2) we get the coercive field close to the transition temperature as

$$e_C = \mp \frac{2}{3} \left[\frac{1}{3(\frac{1}{3} - g)} \right]^{\frac{1}{2}} \left(1 - \frac{T}{T_C} \right)^{\frac{3}{2}} \text{ for TGS, } (6)$$

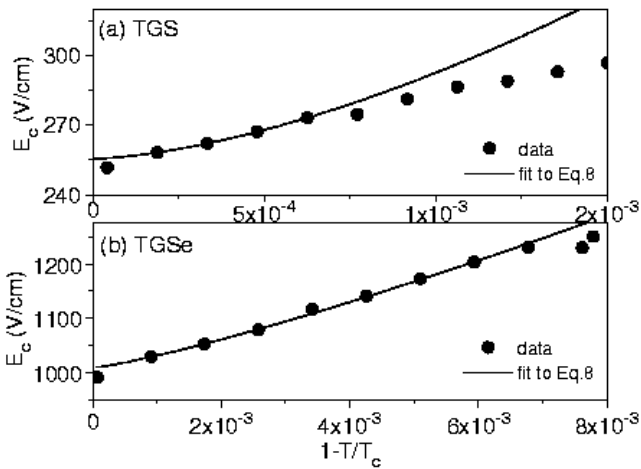


Fig. 2. E_C vs. $(1 - T/T_C)$ in the vicinity of the transition ($T - T_C < 2$ K) for TGS (a) and TGSe (b). Fits to Eq. (8) are also shown.

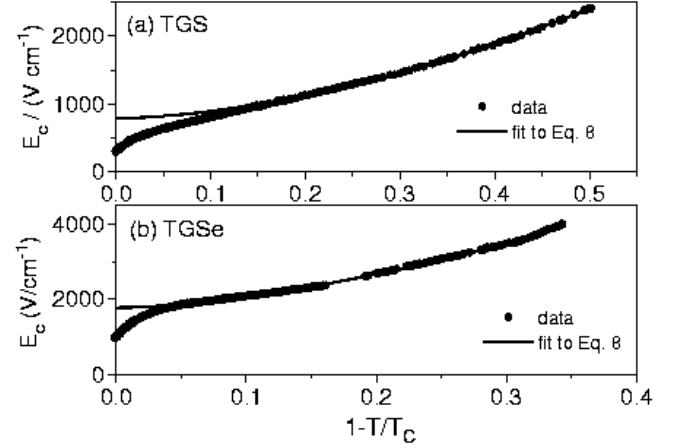


Fig. 3. E_C vs. $(1 - T/T_C)$ for a wide temperature range, more than 100 K below the transition, for TGS (a) and TGSe (b). Fits to Eq. (8) are also shown.

$$e_C = \mp \frac{4}{5} \left[\frac{1}{5(\frac{1}{5} - h)} \right]^{\frac{1}{4}} \left(1 - \frac{T}{T_C} \right)^{\frac{5}{4}} \text{ for TGSe. } (7)$$

Figure 2 shows the observed coercive field of TGS (a)

Table 1. Fit parameters of data in Figs. 2, E_C (ii), and 3, E_C (iii), to Eq. (8). E_C (i) has been fitted with fixed x given by Eqs. (6) and (7).

		E_C (i)	E_C (ii)	E_C (iii)
TGS	A (V/cm)	5.5×10^6	0.2×10^6	4.7×10^3
	x	(3/2)	1.6 ± 0.2	1.4 ± 0.2
TGSe	A (V/cm)	5.2×10^6	9.7×10^4	11.5×10^3
	x	(5/4)	1.2 ± 0.1	1.6 ± 0.2

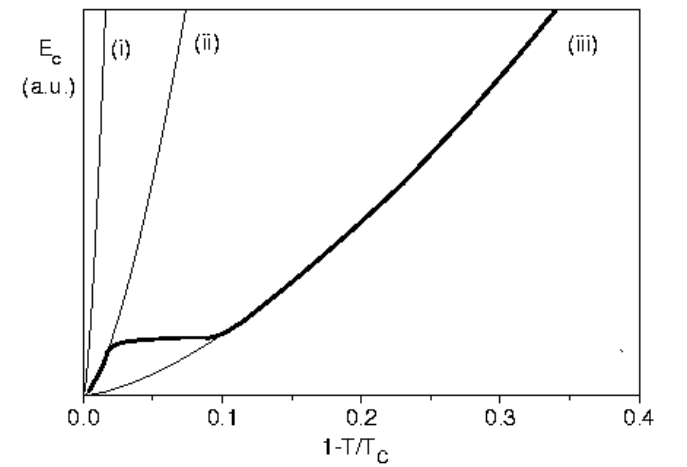


Fig. 4. Schematic plot of $E_C = A(1 - T/T_C)^{3/2}$ for three different switching regimes. A goes down from (i) to (iii), see Table 1. The passing from one to another switching regime is also shown.

and TGSe (b) in the close vicinity of T_C . We can see that

$$E_C \approx C + A \left(1 - \frac{T}{T_C}\right)^x \quad (8)$$

is approximately fulfilled for both crystals in a range at $10^{-4} < (1 - T/T_C) < 10^{-3}$ for TGS and $10^{-4} < (1 - T/T_C) < 10^{-2}$ for TGSe, corresponding presumably to domain wall switching (forward motion) as mentioned below [3]. C is an additive constant which depends strongly on field amplitude, frequency and compensation. This is especially important due to the fact that the exact phase compensation of the loops at $T \approx T_C$ is very difficult to achieve. The coefficient $A = f(\beta) F(g, h)$, where $f(\beta_i) \approx 1$ for bulk switching, being $\beta_i = (E_s/P_s)_i$, $f(\beta_{ii}) \ll 1$ for domain wall switching (forward motion), being $\beta_{ii} = (E_s/P_s)_{ii}$, and $f(\beta_{iii}) \ll f(\beta_{ii})$ for domain wall switching (sidewise motion), being $\beta_{iii} = (E_s/P_s)_{iii}$. We assume that β takes different values (β_i , β_{ii} , β_{iii}) when the temperature is lowered, as shown below. We think that the bulk switching occurs extremely close to T_C and is inaccessible with our experimental conditions. Domain wall (forward) motion occurs at $10^{-4} < (1 - T/T_C) < 10^{-3}$ for TGS and at $10^{-4} < (1 - T/T_C) < 10^{-2}$ for TGSe, and domain wall (sidewise) motion occurs at $0.2 < (1 - T/T_C) < 0.5$ for TGS and at $0.05 < (1 - T/T_C) < 0.3$ for TGSe.

Figure 3 presents the observed coercive fields in a much wider temperature range, $0 < (1 - T/T_C) < 0.5$ and $0 < (1 - T/T_C) < 0.4$ for TGS (a) and TGSe (b), respectively. In the corresponding plots of E_C vs. $(1 - T/T_C)$ we see regions in which, again, we can fit Eq. (8) to the data, this time with $A = A(\beta_{iii}) \ll A(\beta_{ii}) \ll 1$, but this region is outside the validity of the original assumptions and the corresponding exponents do not agree very well with the asymptotic exponents for both crystals. Table 1 shows the results of the fits of Eq. (8) to the experimental data, for TGS and for TGSe. The values

used to substitute into $F(g, h)$ are [2] $g \approx 0.24$ (Eq. (6)) and $h = 0.14$ (Eq. (7)).

Figure 4 shows schematically the behavior of $E_C(T)$ corresponding to three successive switching regimes [3], (i) bulk, (ii) domain wall (forward), (iii) domain wall (side wise), predominant successively as the temperature is lowered. Our results are qualitatively consistent with this general picture, taking into account, as pointed out in the introduction, that the magnitude of the coercive field is strongly dependent on a number of factors of which driving field amplitude and frequency are specially important. Also phase compensation of the loops, made necessarily for a fixed temperature somewhat different from T_C , puts strong limitations to explore region (i).

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